The Photoconversion Mechanism of Excitonic Solar Cells

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Abstract

Excitonic solar cells (XSCs) function by a mechanism that is different than that of conventional solar cells. They have different limitations on their open circuit photovoltages, and their behavior cannot be interpreted as if they were conventional p–n heterojunctions. Exciton dissociation at the heterojunction produces electrons on one side of the interface already separated from the holes produced on the other side of the interface. This creates a powerful photoinduced interfacial chemical potential energy gradient that drives the photovoltaic effect, even in the absence of a built-in electrical potential. The maximum thermodynamic efficiency achievable in an XSC is shown to be identical to that of a conventional solar cell, with the substitution of the optical bandgap in the XSC for the electronic bandgap in the conventional cell. This article briefly reviews the photovoltaic mechanism of XSCs, the limitations on their photovoltage, and their maximum achievable efficiency.

Keywords: efficiency limitations, excitonic mechanism, organic solar cells.

Introduction

Beginning with the advent of the dye-sensitized solar cell (DSSC) in 1990,[1–5] there has been a surge of interest in organic-based solar cells. The DSSC is still the most efficient (up to ~10%), but other designs—ranging from the classical planar p–n junction organic solar cells[6–8] to the newer bulk heterojunction cells[9–13]—are the focus of increasing interest and excitement. All of these cells are what I call excitonic solar cells (XSCs): they function by a fundamentally different mechanism than that of conventional solar cells, a mechanism that is primarily controlled by interfacial processes rather than by the bulk processes that mostly control silicon p–n junctions and other conventional cells.[14–16]

An exciton is a tightly bound electron–hole pair. Excitonic solar cells are a special class of majority carrier devices in which the density of minority carriers is insignificant: that is, electrons are found almost exclusively in one phase (with very few holes) and holes with very few electrons in the other. Excitonic semiconductors are primarily organic materials, but also include a few inorganic materials.[15,16] Charge carriers are generated (and simultaneously separated) at the heterointerface by exciton dissociation, and therefore they also recombine at this interface. (Some bulk generation may occur but this is usually deleterious.) This interfacial mode of carrier generation is fundamentally different from the bulk generation occurring in conventional cells and is responsible for many of the unusual features of XSCs.[15,16] Interfacial properties are of paramount importance in these devices, while bulk properties are less critical. This allows the use of less pure and therefore less expensive materials.

Conventional photovoltaic cells,[17,18] on the other hand, are minority carrier devices in which both electrons and holes coexist in the same chemical phase. Their efficiency is determined primarily by the ability of photogenerated minority carriers (say, electrons in a p-type material) to escape from the p-type region of the device before recombining with the majority carriers. Interfaces are also important in these devices, but the crucial processes of photogeneration, separation and recombination of charge carriers all occur primarily in the bulk material. Therefore, bulk properties such as crystallinity and chemical purity often control the efficiency of conventional solar cells, and optimizing these properties can be expensive.

This article briefly reviews the photovoltaic mechanism of excitonic solar cells, the limitations on their photovoltage, and their maximum achievable efficiency.

Excitonic Solar Cells

Light absorption in organic materials almost always results in the production of a mobile excited state rather than a free electron–hole pair. This occurs for two reasons:[15,16] (1) the attractive Coulomb potential well around the incipient electron–hole pair extends over a large volume because the dielectric constant of the organic phase is usually low, and (2) the non-covalent electronic interactions between organic molecules are weak, resulting in a narrow bandwidth; therefore, the electron's wave function is spatially restricted, allowing it to be localized in the potential well of its conjugate hole (and vice versa). Therefore, a tightly bound electron–hole pair (a Frenkel exciton, or mobile excited state) is the usual product of light absorption in organic semiconductors. It is a mobile, electrically neutral species which, to first order, is unaffected by electric fields. The energy of the initially formed exciton is known as the optical bandgap, E_{opt} (Figure 1).

Electronic trap sites in the bulk can facilitate exciton dissociation into one trapped carrier and one free carrier, but this is not in general a viable mechanism for efficient photoconversion. However, this process does occur to a greater or lesser degree in all XSCs and results in photoconductivity. The more fundamentally important process, and that which drives most XSCs, is the interfacial dissociation of excitons at a heterointerface into a free electron in one material and a free hole on the other side of the interface (Figure 1). Except in DSSCs, excitons must first move, by means of diffusion (and/or relaxation to lower energy states), to the heterointerface before they dissociate by a mechanism that is not yet well understood. The energy of a thermalized (relaxed) singlet exciton, E_{opt}, is less than the bandgap energy of a free electron–hole pair, E_{bg}; the difference being the singlet exciton binding energy (Figure 1). The thermodynamic requirements for interfacial exciton dissociation are obvious—exciton dissociation must be isoenergetic, or downhill; that is, $E_{opt} \geq E_{bg,hj}$ (Figure 1). But the kinetic requirements, and the role of interface polarizability, electric field, exciton transport rates, interfacial electronic states, and so on are not well understood. The crucial process of interfacial charge
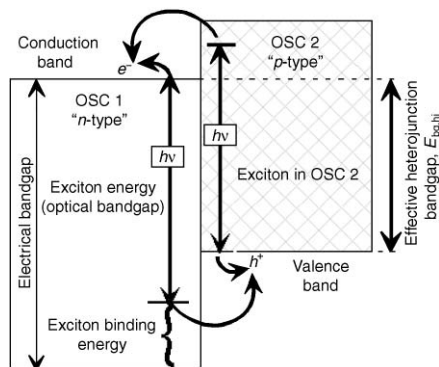
Figure 1. Energy-level diagram for an excitonic solar cell at zero field. Excitons created by light absorption in organic semiconductors 1 and 2 (OSC1 and OSC2) do not possess enough energy to dissociate in the bulk (except at trap sites). But the conduction-band valence-band offsets at the interface between OSC1 and OSC2 provide an exothermic pathway for dissociation of excitons in both phases, producing electrons in OSC1 and holes in OSC2. The band offset must be greater than or equal to the exciton binding energy for dissociation to occur. The three relevant bandgaps are shown: the electrical bandgap, E_{bg}, the optical bandgap, E_{opt}, and the effective bandgap of the heterojunction, $E_{bg,hj}$. The symbol $h\nu$ is the energy of a photon.

carrier recombination is also poorly understood in solid-state organic photovoltaic (OPV) cells, although it is somewhat better characterized at the solid–liquid interface of DSSCs.[19]

Photoconversion Mechanism

Charge carrier generation is simultaneous with, and identical to, the initial charge separation across the heterointerface in illuminated XSCs. This mechanism is very different from the photoconversion mechanism of conventional solar cells. However, at a nonequilibrium thermodynamic (i.e., generalized kinetic) level,[20] all solar cells can be described by the same equations. Employing nonequilibrium thermodynamics, the forces that drive a flux of electrons through a solar cell have been described.[15,16] Gibbs[21] defined the electrochemical potential energy, E, as the sum of the electrical, U, and chemical, μ, potential energies: $E = U + \mu$. The spatial gradient of a potential energy is a force, and ∇E is ultimately the force that drives the particle fluxes through solar cells and other devices. In solar cells, the gradients of the quasi (i.e., nonequilibrium) Fermi levels for each charge carrier, ∇E_{Fn} for electrons and ∇E_{Fp}

for holes, are the forces that drive their respective fluxes.

It is useful to break ∇E_{Fn} into its component quasi-thermodynamic constituents, ∇U and $\nabla \mu$, to reveal the fundamental differences between the photoconversion mechanisms of XSCs and conventional solar cells. The one dimensional current density of electrons, $J_n(x)$, where x is position, through any device is

$$J_n(x) = n(x)\mu_n[\nabla U(x) + \nabla \mu_e(x)], \qquad (1)$$

where $n(x)$ is the concentration of electrons; μ_n is the electron mobility (not to be confused with the electron chemical potential energy, μ_e); and $\nabla \mu_e(x) = k_B T \nabla n(x)/n(x)$, where k_B is the Boltzmann constant and T is the absolute temperature. The terms $\nabla U(x)$ and $\nabla \mu(x)$ in Equation 1 are often referred to as the drift and diffusion components, respectively, of the electron current. One can see immediately from Equation 1 that $\nabla U(x)$ and $\nabla \mu(x)$ are *independent* forces in the photoconversion process and, therefore, that *it is possible to drive a solar cell with either one, or both, of these forces.* In fact, the different types of solar cells can be classified according to the relative importance of these two forces in the photoconversion process.[16]

The photoinduced gradients of the chemical potential energies for electrons and holes, $\nabla \mu_{e,h\nu}$ and $\nabla \mu_{h,h\nu}$, respectively, usually play insignificant roles in conventional photovoltaic cells for two reasons: (1) both electrons and holes are photogenerated together in the same semiconductor phase, and (2) the carrier mobility is high enough for the carrier distribution to "equilibrate" during the carrier lifetime.[16] Therefore, the rule for conventional solar cells is that the built-in electrical potential energy, $\emptyset_{bi}(= \int \nabla U \, dx$ at equilibrium), sets the absolute upper limit to the open-circuit photovoltage, V_{oc}. This occurs because $\emptyset_{bi}$ is *required* for charge separation. In XSCs, however, the charge carrier pairs are already separated across an interface upon photogeneration, generating a large $\nabla \mu_{h\nu}$ (Figure 2), which by itself is a powerful photovoltaic driving force. In solid-state XSCs, ∇U also plays a role, but it is no longer the only driving force and is often subordinate to $\nabla \mu_{h\nu}$. For this reason, qV_{oc} (where q is the electronic charge) is often larger than $\emptyset_{bi}$ in XSCs. In DSSCs, where ∇U is almost entirely screened by the mobile electrolyte, V_{oc} is controlled almost entirely by $\nabla \mu_{h\nu}$.[15,22] Thus, in general, the photovoltage of a solar cell is a function of *both* electrical *and* chemical potential energy differences. The common assumption that $\emptyset_{bi}$ alone sets the absolute upper limit to the photovoltage is not true.
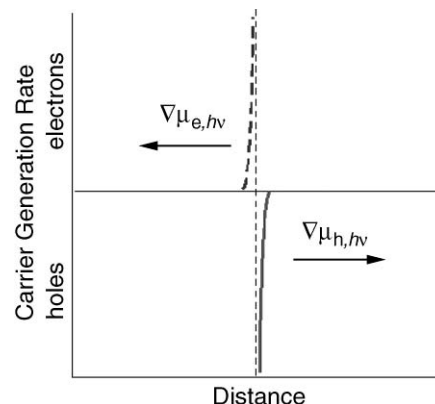

Figure 2. In excitonic solar cells (XSCs), electrons are photogenerated on one side of the heterojunction, while holes are generated on the other by means of interfacial exciton dissociation (the phase boundary is denoted by the vertical dashed line). Carrier photogeneration is simultaneous to, and identical with, carrier separation across the interface in XSC cells; the chemical potential energy ($\nabla \mu_{h\nu}$) values therefore drive electrons and holes in opposite directions.

The $\nabla \mu$ component plays a role in the current flow of all devices, but its importance declines as the equilibrium carrier concentration increases. In metals, for example, the carrier concentration is so high that no significant concentration gradients can be achieved. In highly doped semiconductors, significant values of $\nabla \mu$ can be achieved only in the minority carrier density. One reason for the importance of $\nabla \mu$ in XSCs is the very low equilibrium charge density in most organic materials.

Maximum Theoretical Efficiency of XSCs

In a classical paper, Schockley and Quiesser determined the maximum theoretical efficiency, η_{max}, for conventional solar cells.[23] They calculated the three efficiency-determining factors, V_{oc}, the short-circuit current density (J_{sc}) and fill factor (*FF*) as a function of bandgap, and then optimized their product. The minimum possible exchange current density (reverse diode current density, J_0) was obtained by considering the semiconductor's equilibrium absorption and emission of black-body radiation. This provided estimates of V_{oc} and *FF*. The maximum possible photocurrent was easily obtained by the overlap of the solar flux spectrum with the idealized semiconductor absorption spectrum. This analysis led to the conclusion that the maximum efficiency of a single-bandgap (homojunction) solar cell

under 1 sun (AM 1.5) illumination was ~31% for a bandgap of 1.4 eV.

In the conventional semiconductors considered by Schockley and Quiesser (hereafter, S&Q), the optical and electrical bandgaps are identical. This is not the case in XSCs. However, S&Q's approach is applicable to the standard XSC heterojunction (Figure 1) by making the following two substitutions for E_{bg}: It is E_{opt} in XSCs that controls the light absorption; and it is $E_{bg,hj}$ that determines the standard free energy of electron–hole pairs in a heterojunction cell (Figure 1). Thus, in the ideal case where $E_{opt} = E_{bg,hj}$ in both semiconductors, the energetics are formally equivalent to the $p–n$ homojunction treated by S&Q, and therefore, the efficiency limit is identical to the S&Q limit (but substituting E_{opt} for E_{bg}).

This ideal case assumes that no enthalpy is required for exciton dissociation. Entropy favors dissociation because one bound electron–hole pair is converted into two free carriers. Any electric field present at the junction would also favor dissociation. Realistically, however, some decrease in enthalpy may be required for exciton dissociation, but so far there is little theoretical or experimental understanding of the minimum energetic requirements. Clearly, the energy difference between E_{opt} and $E_{bg,hj}$ will be irreversibly lost to the photoconversion process, regardless of what mechanisms are involved. Also, in actual XSCs, there is often a relaxation from the initially formed state at an energy of E_{opt} to a lower electronic state, which may be a triplet state or a polaron or bipolaron state (one or two charges stabilized by lattice relaxation). The exciton then dissociates from this lower energy level. If all else were equal, solar cells that employed triplet states or polaronic states would have a lower maximum efficiency limit than those in which the excitons remained at the energy of E_{opt}. The

common notion that the exciton binding energy affects the maximum theoretical efficiency, however, is incorrect; this energy plays no role in the efficiency calculations.

Summary

The characteristic that distinguishes excitonic solar cells from conventional solar cells is that charge carrier generation and separation are simultaneous and occur by exciton dissociation at a heterointerface. Electrons are photogenerated on one side of the interface and holes on the other. This contrasts with the spatially and temporally distinct processes of carrier generation in the bulk and subsequent separation in conventional solar cells. The carrier generation/separation mechanism in XSCs produces a powerful chemical potential energy gradient, $\nabla \mu_{hv}$, that drives the photovoltaic effect, even in the absence of, or in opposition to, a built-in electrical potential energy difference, $\emptyset_{bi}$. While the maximum photovoltage achievable in conventional solar cells is limited to less than $\emptyset_{bi}$, it is experimentally observed, and theoretically expected, to be often substantially greater than $\emptyset_{bi}$ in well-designed XSCs. Despite these differences, the maximum theoretically obtainable efficiency for XSCs is given by the Schockley–Quiesser limit, as it is for conventional solar cells, with the substitution of the optical bandgap in XSCs for the electrical bandgap in conventional cells.

Acknowledgments

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